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| Fractional Distillation |
| A beginners guide to concepts in small and large scale fractional distillation |
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Distillation is the process of separating a liquid mixture into its parts. The first recorded events of distillation go back to Alexandria in the first century A.D. The Arabic alchemists knew of distillation from the Egyptians before them and the philosopher Alexander of Aphrodisias wrote of it around 200 A.D. The process has since been adapted to suit the separation of just about any combination of liquids imaginable. Some of these needs can be accomplished on a small scale in the laboratory. Others, such as the separation of crude oil into its major components, are done on such a large scale that revision to technique is needed. To this end, much large scale distillation is executed under the modified principles of small scale distillation. The mathematics and general principles are very similar, but the equipment and methods of control are drastically different. In this paper I hope to point out the general similarities and differences between the two.

The intended outcome of distillation is the separation of a mixture by utilizing the differing boiling points of each component to separate the compound into its parts. When a heterogeneous mixture is composed of parts with a wide difference in boiling points, simple distillation can be repeated to produce higher purity product. When separating a mixture of closely differing boiling points, fractional distillation can be utilized, as the process of fractional distillation amalgamates several cycles of simple distillation into one process.

Assume a heterogeneous mixture is composed of pure compounds higher temperature boiling A and lower temperature boiling B. The process begins in the pot. Here the temperature is raised to just above the boiling point of A. As the mixture begins to boil, gas composed of A and B is formed. Travelling up the column, the cooler temperature causes the gas to condense onto the sides and packing inside the column. The liquid gets warmer running back towards the heated pot and some of it evaporates again. This time, however, the gas is composed of more B than A, as the lower boiling point B leaves in higher quantities than A. This process repeats until the gas reaches the head of the column, where the gas (if the distillation is done properly) is almost pure B. The gas goes down a tube that promotes condensation and the liquid B is collected at the end.

Each cycle of evaporation and condensation along a section of the distillation column is called a theoretical plate. The greater the number of theoretical plates means greater purity in the yield. The number of theoretical plates is calculated by the Fenske equation:

N= [log(ZA/XA) – log(ZB/XB)]/ log α

N = the number of theoretical plates; X=the mole fraction of the liquids in the distilland; Z=the mole fractions at the head of the column and α=the relative volatility of the two liquids. Of particular importance is the relative volatility (α) of the two liquids. The equation for relative volatility is:

α = (Yi/Xi)/(Yj/Xj) = Ki/Kj

Where Yi & Yj = the vapor-liquid equilibrium of the components i and j in the *vapor* phase[3]

Xi & Xj = the vapor-liquid equilibrium of the components i and j in the *liquid* phase[3]

Reflux is the process by which liquid that is condensed is returned to the source of heat. The rate that this reflux occurs is of particular importance as each reflux cycle produces more of the less volatile material to the heat source separated from the more volatile component. The equation for reflux is as follows:

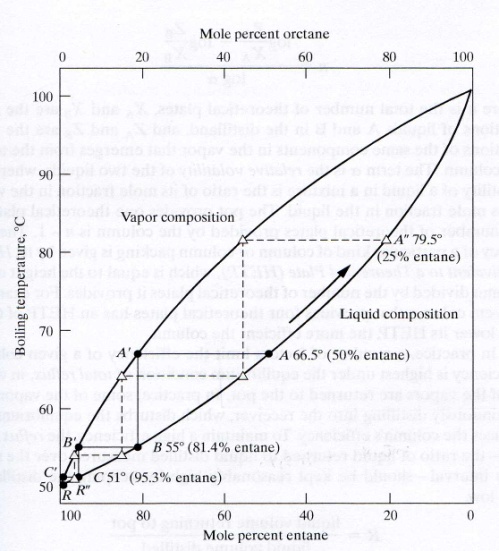
Reflux Rate = Liquid returning to the pot/liquid volume distilled

A rule of thumb is that the reflux rate should be at least equal to the number of theoretical plates.[6] As reflux represents one cycle of simple distillation, the separation process produces best results with higher reflux rates. Economic, energetic and time concerns, however, are usually deterrents to utilizing many reflux cycles in large scale distillation and the reduction of reflux rates is of key concern in the design of these towers.

The Height Equivalent to a Theoretical Plate (HETP) is a method of determining the efficiency of the column and its packing. The equation for the HETP is:

HETP = column height/number of theoretical plates (from the Fenske equation)

The lower the HETP, the more efficient the column as each theoretical plate represents the length of column that one reflux occurs on.

As distillation proceeds, the results are not an entire separation of the components. This graph of two ideal fictitious liquids orctane, boiling point 100˚C at the top of the graph and entane, boiling point 50˚C at the bottom of the graph. The curves represent the liquid/vapor composition at varying temperatures. As noted at point A there is 50% entane in the liquid but 80% entane in the gas being condensed and at about 55˚C, 80% entane is in liquid and more than 95% entane in the vapor being condensed. As you can see, careful consideration of distillation temperature as distillation occurs is also of key importance. Orctane and entane are two ideal liquids and no liquid behaves ideally. In real life situations, there is usually an azeotrope, where at a certain temperature and percent compostition in the distilland the reverse effect of distillation occurs. There are tables that chemists use to locate these points in a mixture and planning work arounds for azeotropes is also a consideration in the distillation process.

Using these facts and equations, we should be able to set up the conditions necessary to distill a mixture. To make things simple we will set up an ideal (not real) mixture in order to understand the principles of the real thing. Consider the following data.



“A” is the more volatile component of the mixture. Equilibrium pressures of various compounds at various temperatures are available on the internet, Perry’s Chemical Engineers Handbook and many other sources. The above data was obtained by modifying Raoults Law and Dalton’s law to obtain the equations

Mole fraction A in liquid = [P-VP(B)]/[VP(A)-VP(B)]

Where P = 760torr (pressure of the more volatile component at its normal boiling point)

VP(argument) = The vapor pressure of the argument at a given temperature

~and~

Mole fraction A in vapor = [VP(A)/pressure at normal BP of A] [Mole fraction of A in liquid]

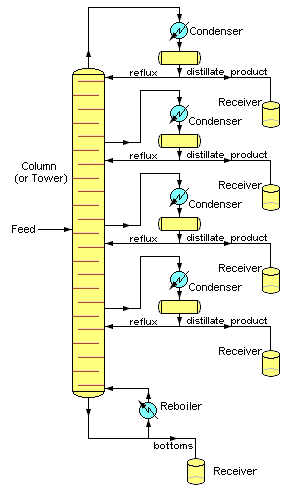
From there we can subtract these values from 1 and get the mole fractions of B. In our perfect world with our perfect distillation of ideal liquids, the number of theoretical plates by the Fenske equation is 1(can you see why? Hint: write out the whole equation and remember that subtraction of logarithms is actually division). Actually, it is zero, as the pot at the bottom of the column acts as the first theoretical plate so the number of theoretical plates in the column is = N-1. However, there are no ideal compounds waiting for perfect distillation at perfect reflux rates (where all of the liquid is returned to the pot). As noted below, the number of actual plates needs to be more than the number of theoretical plates needed per the equation:

Na = Nt/E

In our perfect world Nt and E would be 100% and Na would be 1. And from the above calculations this is true. But in the real world we could consider the following. If the column was 90% efficient at 70 ˚C, then the mole fraction of “A” in the first few drops distilled (and the indication of the mole fraction at this temperature of the vapor at the head of the distillation column) would be 0.684 and the mole fraction of “B” would be .267. Adjusting the mole fraction in the liquid to suit the amount in the gas and running the Fenske equation, we get 1.05 as the number of theoretical plates and the number of actual plates equal to 1.16. Now, to get further into reality, remember that a bit of the initial product will be lost in holdup along the column packing and walls; imperfect control of temperature will skew data; imperfect reflux rates will send less than ideal vapor mixtures to the head of the tower etc. The initial readings will be far from perfect. But if the liquid is raised in temperature a little at a time and careful attention is paid to maintaining a high reflux ratio, and the first sample condensed is a small sample, you can estimate about a 60% efficiency to start and see if the gas chromatography results bear it out. Technique can be adjusted after running the equation with this information to triangulate to better yeilds.

Another way to approach the problem is to estimate how many theoretical plates would provide a desired HETP. Algebraically manipulating the Fenske equation (its just an equation, play with it all you like) to suit, you can find and plug in your theoretical yield and go from there.

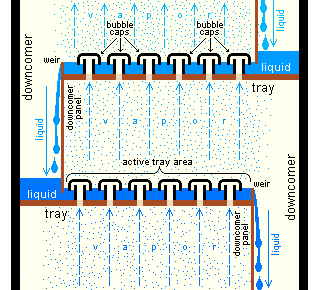
Putting all of this together, one can mathematically design a process over time using the volatilities of the two liquids to be separated, the Fenske equation, desired reflux rates and the HETP along with known thermodynamic properties of the materials being separated to construct a process by which desired yields can be produced. And this is exactly what is done in large scale distillation, with some modification to the process.

Distillation to produce and refine hydrocarbons uses these basic ideas modified to fit large scale production. Distillation columns sixty meters high are not uncommon in refineries. The breakdown of crude oil into its components is one of the unit operations of chemical engineering, meaning it is one stage of a multistage process. This process is an example of continuous distillation where crude is fed into the fractional column continuously and the fractions removed continuously from the output stream. It is important to note that these fractions are not composed of one material of one boiling point, but of several materials within a close range of boiling points. Each of these fractions are then sent to be further refined as current market conditions dictate.

Unlike our simple packed column, this column has trays incorporated into areas that can be independently refluxed with multiple condensation and collection points.

The crude is fed into the feed section in the middle of the column. The less volatile chemicals begin to separate from the more volatile components and move downwards with the heaviest reaching the bottom of the column. This is called “stripping” as the more volatile components are “stripped” from the less volatile ones. Eventually, the heaviest compounds of the highest molecular mass reach the bottom. This forms what is called “bottoms.”

As the makeup of the incoming crude is of differing chemical makeup from one cubic meter to the next, its separation into parts is a dynamic situation. If the materials at the end of a system of trays is condensed and deemed to not meet a purity standard, it is sent back into the column to be refluxed. Here, more of the heavier materials fall lower in the column and more volatile materials vaporize higher. When the target fraction is acceptable, refluxing is discontinued and the condensed liquid is sent to a receiver. In essence, it is as though multiple fractional distillations as we know it in the lab are being done simultaneously with continuous feed into the pot.

Of note are the trays that the distillate collects in, as they are central to large scale distillation, as diagrammed to the right. Note how each active tray area is a collection point for more volatile material from below and less volatile material from above. A collection of these trays creates a dynamic continuous cycle area in which pressure and temperature can be controlled by the operator to adjust the number of refluxing cycles necessary to produce the fractions desired.

Any surface that provides contact with liquid or vapor in a large scale distillation is called a “plate” or “tray.”[2] A theoretical tray or plate is a mathematical “go between” to bridge calculations between the theoretical and actual necessities of the column. Expanding on the concept of efficiency in calculating the HETP comes the expression:

Na = Nt/E

Where Na= the number of actual physical plates and trays; Nt = the number of theoretical plates or trays and E= the tray or plate efficiency. As nothing is 100% efficient, the number of actual plates needs to exceed the number of theoretical plates or trays to arrive at projected theoretical yields.

In designing a column, this equation is a jump off point to setting up the equations necessary to produce a mathematical model of maximum efficiency for the column. The design of a column that produces a distillate flow that is both cost efficient and time minimizing is the brass ring. As noted before, unlike our lab columns, operators and computers adjust the conditions inside the reflux area to keep the incoming dynamic stream in line with this theoretical distillate flow in order to obtain the target of maximum efficiency.

The Fenske equation is applicable in large scale distillation; however its components must be modified to fit the situation. Remember that the fractions obtained are a mixture of components of close volatility. Also recall from the definition of α from above that K is a function of temperature and pressure as vapor pressures are measured at specific values of T and P. In Perry’s Chemical Engineers handbook, the suggestion on page 13-9 is that “an alternative measure of composition is the convergence pressure of the system, which is defined as that pressure at which the K values for all of the components in an isothermal mixture converge to unity. It is analogous to a critical point for a pure component in the sense that the two phases become indistinguishable.” What this means is that a mixture of chemicals behaving in like manner at a given temperature and pressure can be given one K value. With this in mind, the Fenske equation can be given, the definition modified as follows:

N= [log(ZA/XA) – log(ZB/XB)]/ log α

N = the number of theoretical plates; X=the mole fraction of the liquids in the distilland; Z=the mole fractions at the head of the column and α=the relative volatility of the two liquids. A and B are the distillands and bottoms respectively.

Using these values for K allows the use of the identical equation for α, where i and j are the distilland and the bottoms respectively:

α = (Yi/Xi)/(Yj/Xj) = Ki/Kj

Where Yi & Yj = the vapor-liquid equilibrium of the components i and j in the *vapor* phase[3]

Xi & Xj = the vapor-liquid equilibrium of the components i and j in the *liquid* phase[3]

An example of a fraction of crude oil distillation is naptha or white gasoline. Light naptha is considered to be the fraction consisting of 5-6 carbons with a boiling point range from 30˚C to 90˚C. Heavy naptha boils between 90˚C to 200˚C and has 6-12 carbons per molecule. As evidenced by the range in the boiling point, the molecular variety that makes up naptha is varied. These ranges may seem extreme (especially when considering our lab experiment conditions) however considering the scale of the tower and energy put into producing light naptha at the upper part of the tower, the fraction can be considered to be approaching one value for vapor pressure at given temperatures. In this manner Napta and other heavier fractions such as kerosene (BP 150-275˚C made of 6-16 carbon molecules) may be separated using the same theories and concepts as out small scale experiment, albeit with a 60meter tower and computer control of the conditions inside the tower. Naptha and kerosene as fractions may be further refined in a separate unit operation or sold as is, depending on market conditions.

As distillation on such a large scale is a huge energy concern, primary consideration is given to market conditions as the driving factor as to whether or not a chemical should be separated at all. In such cases, the Fenske equation can be a quick and dirty way to determine whether to proceed with distillation. In the petrochemical industry, there are general distilling conditions that are considered economically viable. If the relative volatility of any fractions to be separated is less than 1.05, it will be necessary to reflux the liquid many times and is generally considered to not be economically viable. It is suggested the reflux ratios of 1.2 to 1.5 times the minimum reflux ratio suggested for the column as reflux in this range generally is cost lowering overall.[4] This is a rule of thumb of course and abnormalities in the conditions that make that rule true may exist.

While the uses of distillation are certainly not limited to the products in this discussion, represented are two ends of the spectrum of distillation uses by scale. It is my hope that this paper provides a link to the beginning chemist’s view to a wider scope of the technique.

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